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PREPARATION OF PYRIDYL-SUBSTITUTED MONOAZATRIPHENYLENES

D. S. Kopchuk[1,2], G. V. Zyryanov[1,2]*, I. S. Kovalev[1], A. F. Khasanov[1], A. S. Medvedevskikh[1], V. L. Rusinov[1,2], and O. N. Chupakhin[1,2]

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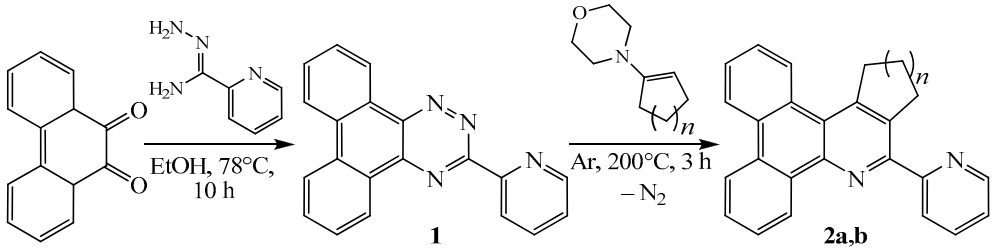
Azatriphenylene derivatives are of considerable interest due to their promising photophysical and coordinating properties [1] and to their presence in the composition of natural compounds [2, 3]. Azatriphenylenes are important in inorganic biochemistry thanks to their use as intercalating ligands [4, 5]. In addition, azatriphenylenes have shown promise as luminescent chemosensors of organic anions and nitroaromatic compounds [6].

The most frequently used method for preparing azatriphenylenes is the Skraup synthesis [7, 8] which demands the use of forcing conditions. Contemporary synthetic methods broadly use a cycloaddition reaction of hard to obtain alkenes or arylacetylenes with aromatic substrates catalyzed by transition metal salts [9, 10]. Finally, the cyclocondensation of phenanthrenequinone with hydrazones of (hetero)aromatic carboxylic acid amides leads to the corresponding aryl- [11, 12] and hetaryl-substituted [13] triazatriphenylenes.

In this report, we propose an efficient method for the synthesis of cycloalkene-annelated derivatives of monoazatriphenylenes based on an aza-Diels–Alder reaction of the previously uncharacterized 3-(pyridin-2-yl)phenathro[9,10-*e*][1,2,4]triazine (**1**) [14] with 1-morpholinocycloalkenes. A method for preparing different pyridine derivatives through reaction of the corresponding mononuclear 1,2,4-triazines has been known for some time [15-17]. In our work, we have used this method for the first time in a single-stage synthesis of the poorly available pyridyl-substituted monoazatriphenylenes **2a**,**b**.



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a $n = 1$, **b** $n = 2$

2a,**b**

*To whom correspondence should be addressed, e-mail: gvzyryanov@gmail.com.

[1]Ural Federal University named after the First President of Russia B. N. Yeltsin, 19 Mira St., Yekaterinburg 620002, Russia.

[2]I. Ya. Postovskii Institute of Organic Synthesis, 22 Akademicheskaya/20 S. Kovalevskoi St., Yekaterinburg 620219, Russia; e-mail: chupakhin@ios.uran.ru.

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For the preparation of compounds **2a**,**b**, we have synthesized the corresponding triazatriphenylene **1** by direct heating of phenanthrenequinone with the pyridine-2-carboxylic acid amide hydrazone. The corresponding monoazatriphenylenes **2a**,**b** were prepared by heating compound **1** in the presence of a fivefold excess of the corresponding enamine at 200ºC without solvent. The structures of the obtained compounds were confirmed by ^{1}H and ^{13}C NMR, and mass spectrometry and from elemental analytical data. Thus, the ^{1}H NMR spectra of compounds **2a**,**b** show characteristic signals for the cycloalkene fragments as multiplet and triplets in the range 1.70-3.60 ppm and also signals for the aromatic fragments at 7.00-9.50 ppm. The mass spectra of compounds **2a**,**b** show molecular ion peaks corresponding to the proposed structure.

Preliminary experiments to study the complex-forming properties of the obtained products have shown a high potential of the monoazatriphenylenes **2a**,**b** as ligands for transition metal cations.

Therefore, using an aza-Diels–Alder reaction we have, for the first time, carried out a single-stage synthesis of the poorly available pyridyl-substituted monoazatriphenylenes as promising ligands for transition metal cations.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-400 instrument (400 and 100 MHz, respectively) using $CDCl_3$ with TMS as internal standard. Mass spectra (electrospray ionization) were recorded on a Bruker Daltonics microTOF-Q II mass spectrometer. Elemental analysis was carried out on a Perkin-Elmer PE 2400 series II CHN analyzer. Melting points were determined on a Boetius melting point apparatus. TLC analysis was performed on Merck 60F254 silica gel plates and revealed using UV light. The pyridine-2-carboxylic acid amide hydrazone was prepared by a reported method [18].

3-(Pyridin-2-yl)phenanthro[9,10-*e*][1,2,4]triazine (1). Phenanthrenequinone (1 g, 4.81 mmol) was dissolved in ethanol (100 ml), and the pyridine-2-carboxylic acid amide hydrazone (0.65 g, 4.81 mmol) was added. The mixture was refluxed for 10 h, and the precipitate formed was filtered off, washed with ethanol, and dried. Yield 0.83 g (56%). Yellow crystals; mp 202-204ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.54 (1H, m, H-5 Py); 7.73-7.93 (4H, m, H Ar); 8.01 (1H, td, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.59 (2H, m, H Ar); 8.89 (1H, dd, ^3J = 7.5, ^4J = 1.2, H-3 Py); 9.01 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.47 (1H, dd, ^3J = 8.0, ^4J = 1.2, H-5); 9.53 (1H, dd, ^3J = 8.0, ^4J = 1.2, H-12). ^{13}C NMR spectrum, δ, ppm: 122.9 (2C); 124.3; 125.1; 125.2; 127.0; 127.4; 127.7; 128.0; 128.5; 130.9; 131.2; 132.4; 133.7; 137.1; 143.1; 145.4; 150.5; 153.7; 160.5. Mass spectrum, *m*/*z* (I_{rel}, %): 309.11 $[M+H]^+$ (100). Found, %: C 77.83; H 3.79; N 18.02. $C_{20}H_{12}N_4$. Calculated, %: C 77.91; H 3.92; N 18.17.

Synthesis of Monoazatriphenylenes 2a,b (General Method). A mixture of triazatriphenylene **1** (0.4 g, 1.3 mmol) and the corresponding 1-morpholinocycloalkene (6.49 mmol) was stirred under an argon atmosphere at 200ºC for 2 h. An additional portion of the 1-morpholinocycloalkene (3.25 mmol) was added, and the mixture was stirred at 200ºC for a further 1 h. The reaction mixture was cooled to room temperature, acetonitrile (30 ml) was added, and stirring continued for 3 h. The precipitate formed was filtered off, washed with acetonitrile, and dried.

10-(Pyridin-2-yl)-12,13-dihydro-11*H*-dibenzo[*f*,*h*]cyclopenta[*c*]quinoline (2a). Yield 0.35 g (78%). Colorless crystals; mp 181-183ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25 (2H, m, 12-CH_2); 3.63 (2H, t, ^3J = 7.2, 11-CH_2); 3.73 (2H, t, ^3J = 7.2, 13-CH_2); 7.33 (1H, m, H-5 Py); 7.62-7.74 (4H, m, H Ar); 7.92 (1H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.60 (1H, m, H-3 Py); 8.63-8.77 (4H, m, H-6 Py, H Ar); 9.51 (1H, m, H-8). ^{13}C NMR spectrum, δ, ppm: 26.1; 33.2; 37.4; 122.4; 122.9; 123.1; 123.3; 123.7; 126.1; 126.6; 127.2; 127.3; 127.7; 128.3; 130.1; 130.8; 131.1; 131.8; 136.4; 138.9; 144.9; 148.5; 150.3; 151.9; 158.9. Mass spectrum, *m*/*z* (I_{rel}, %): 347.15 $[M+H]^+$ (100). Found, %: C 86.52; H 5.11; N 7.88. $C_{25}H_{18}N_2$. Calculated, %: C 86.68; H 5.24; N 8.09.

10-(Pyridin-2-yl)-11,12,13,14-tetrahydro-11*H*-dibenzo[*f*,*h*]cyclohexa[*c*]quinoline (2b). Yield 0.32 g (68%). Colorless crystals; mp 174-176ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.71-1.74 (2H, m, $ArCH_2C\underline{H}_2$); 1.93-1.96 (2H, m, $ArCH_2C\underline{H}_2$); 3.23 (2H, t, ^3J = 7.1, 11-CH_2); 3.53 (2H, t, ^3J = 7.1, 14-CH_2); 7.36 (1H, m, H-5 Py); 7.56-7.72 (4H, m, H Ar); 7.92 (1H, ddd, ^3J = 7.5, ^3J = 7.5, ^4J = 1.8, H-4 Py); 8.08 (1H, m, H Ar); 8.50-8.58 (2H, m, H-3 Py, H Ar); 8.68 (1H, m, H Ar); 8.72 (1H, dd, ^3J = 4.9, ^4J = 1.8, H-6 Py); 9.30 (1H, m, H-8). Mass

spectrum, *m*/*z* (I_{rel}, %): 361.17 $[M+H]^+$ (100). Found, %: C 86.48; H 5.45; N 7.46. $C_{26}H_{20}N_2$. Calculated, %: C 86.64; H 5.59; N 7.77.

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